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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Water Treatment Blend in Solid Form

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WATER TREATMENT BLEND IN SOLID FORM

Abstract of the Disclosure

There is now provided a water treatment blend in solid form for disinfection and bacteriological stabilization of aqueous media. The solid is an intimate blend of solid particulates and can provide
5 prolonged release of both chlorine and bromine in aqueous media. The blend contains one or more alkali metal or alkaline earth metal hypochlorite with one or more N-halogenated dialkylhydantoin. The solid composition can combine excellent shelf stability with
10 desirable disinfection property in use. A blend of calcium hypochlorite with 1-bromo-3-chloro-5, 5-dimethylhydantoin is especially preferred.

WATER TREATMENT BLEND IN SOLID FORM

BACKGROUND OF THE INVENTION

Compositions which release chlorine into aqueous media have been found to be generally useful, such as for preparing a sterilizing solution. For example it has been taught in U.S. Patent No. 4,104,024 to
5 sterilize an article at a temperature below that of boiling water with a sterilizing solution having active chlorine. A variety of ingredients have been proposed for such a sterilizing solution. These ingredients include hypochlorite salts, toluene
10 sulfochloroamide compounds, chlorine dioxide, chlorinated hydantoin, and trichloroisocyanuric acid and salts thereof.

Chlorine-containing compositions may also be utilized for treatment of specific media, e.g.,
15 swimming pools. In such use, compounds can be provided in a dispenser and the chemicals for water treatment thereby dispensed to the swimming pool.

Suitable chlorine donor chemicals that have been disclosed, e.g., in British Patent No. 1,327,763,
20 include the chlorocyanuric acids, calcium hypochlorite and the halogenated hydantoins. It has also been known to provide a chemical dispenser of disinfecting agent

for a toilet tank. As disclosed in U.S. Patent No. 4,709,423 such a dispenser for providing a disinfectant solution may contain a disinfectant such as halogenated hydantoin, trichloroisocyanuric acid, and inorganic hypochlorite salts, e.g., the salts of calcium, lithium and magnesium.

Compositions providing available chlorine may also be useful in dishwasher detergent compositions. Thus there has been disclosed in U.S. Patent No. 4,284,524 a cleaning composition for automatic dishwashers, which composition can contain available chlorine at a level of from about 0.5 to about 3 percent. To provide the available chlorine, there may be used chlorinated trisodium phosphate as well as other materials such as chloroisocyanurates, chlorinated hydantoin, toluene sulfodichloroamides, hypochlorite salts, chlorinated melamine, chlorinated succinimide, or N-chloroacetyl urea and the like.

It has usually been proposed to provide various blends or mixtures of ingredients for these specific treating composition. For example U.S. Patent No. 4,709,423 recommends a mixture of trichloroisocyanuric acid plus cyanuric acid. British Patent No. 1,327,763 recommends a mixture containing cyanuric acid or salt thereof. U.S. Patent No. 3, 629,408 discloses a combination of hypochlorite salt with a chlorinated glycoluril.

It would however still be desirable to provide a disinfectant composition that combines a great variety of desirable characteristics, e.g., economy of manufacture, enhanced disinfectant quality and controlled dissolve rate.

SUMMARY OF THE INVENTION

There has now been devised a water treatment

composition, in solid form, having much sought after disinfection characteristics for aqueous media. If desired, the composition will provide prolonged, controlled dissolve rate to such media. Moreover, the composition can exhibit viricidal properties in use, combined with extended shelf stability before use. The composition furthermore has suitable low toxicity in handling, storage and use.

In one aspect, the present invention is directed to a new composition of matter comprising a solid composition in the form of particles blended together of one or more alkali metal or alkaline earth metal hypochlorite with one or more N-halogenated dialkylhydantoin. A particularly preferred blend is calcium hypochlorite with 1-bromo-3-chloro-5,5-dimethylhydantoin.

In another aspect the invention is directed to the method of treating an aqueous media to provide available chlorine to such media.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The composition of the present invention can be used for treating a variety of fluid media. For example in water treatment, it may be used generally to provide available chlorine to media containing biologically active components such as bacteria and viruses, e.g., it may be utilized for treating aqueous sewage media, plant effluent, cooling towers, lagoons and secondary water recovery. The composition can also be used for specialty water treatment, e.g., in swimming pools. In general, the composition will be utilized for providing available chlorine to media for bleaching, sterilizing and disinfecting applications.

The composition will provide available chlorine to the media to be treated. It is to be understood that

the composition might not only dispense available chlorine, but may also provide bromine. Whether the composition provides chlorine or bromine or both, for purposes of convenience, unless otherwise expressly
5 detailed, this will be referred to hereinafter simply as available chlorine. It will thereby be understood that when the word "halogen" is used herein, such will refer to chlorine, bromine, or both.

The available chlorine is expressed as the amount,
10 as a percentage, of the halogen, i.e., chlorine or bromine or both, that is available based upon the total of such halogens present in the solid composition. This availability may be determined by titration of an aqueous solution of the composition, such as with sodium
15 thiosulphate. This available chlorine may therefore also be referred to as titratable chlorine. Although providing a high degree of available chlorine, the composition of the present invention has a most desirable low toxicity. Yet it will nevertheless
20 provide excellent disinfection as well as viricidal characteristics while providing for bacteriological stabilization of aqueous media.

The hypochlorite, which may also be referred to herein as the hypochlorite salt, will be an alkali metal
25 or alkaline earth metal hypochlorite. The metal of the salt will most often be sodium, potassium, lithium, calcium or magnesium. Mixtures of these salts may also be used, such as mixtures including alkali metal plus alkaline earth metal salts, e.g., lithium hypochlorite
30 mixed with calcium hypochlorite. Preferably for economy of the composition as well as efficiency of available chlorine, the hypochlorite salt will simply be calcium hypochlorite. In the blended, solid composition the hypochlorite salt can be expected to provide from about
35 65 to 75 percent available chlorine, or about 55 to 75 percent available chlorine in the composition.

The hydantoin used will be an N-halogenated dialkylhydantoin. The halogen for this hydantoin will be one or more of chlorine or bromine. For example, there may be used 1-bromo-3-chloro-5,5-dimethylhydantoin (which may be referred to hereinafter simply as "BCDMH"). Advantageously for economy, the alkyl of the dialkylhydantoin will be either or both of methyl or ethyl. For example there may be supplied as the hydantoin 1,3-dichloro-5-ethyl-5-methylhydantoin. The hydantoin used can be expected to provide from 48 to 72 percent available chlorine or about 0.5 to 18 percent available chlorine in the composition as either bromine or chlorine or both. In addition to the hydantoins mentioned above, other suitable compounds that may be used include 1,3-dibromo-5,5-dimethylhydantoin and 1,3-dichloro-5,5-dimethylhydantoin. Additionally, mixtures of hydantoins may be utilized in the composition. For example a mixture containing a minor amount of 1,3-dichloro-5-ethyl-5-methylhydantoin may be useful where the major portion of the mixture is supplied by 1,3-dichloro-5,5-dimethylhydantoin. It is to be understood that for economy the hydantoins that will be used will most always be the commercially available materials that can range from about 90 to more than 99 percent active ingredient, with a balance typically of incidental inerts. Preferably for efficient dispensing of available chlorine, the hydantoin used will be BCDMH.

The hypochlorite salt may be available in powder or flake form. However, other particulate, solid form, e.g., granules, can be particularly serviceable, especially where such are comminuted prior to use. Usually, for blending with the hydantoin, the hypochlorite salt will be a free-flowing particulate having particle size within the range from about 12 to about 100 mesh. Hypochlorite salt more finely divided than about 100 mesh can lead to problems such as dusting

when blending with the hydantoin. Salt particles of greater size than about 12 mesh will most always detract from obtaining a uniform blend of the solid particulates. Preferably, for best blending the
5 hypochlorite salt will be a granular material having a particle size within the range of from about 16 mesh to about 40 mesh.

The hydantoins are usually commercially available as dry, free-flowing solids in powder or granular or
10 flake form. Typically, as with the hypochlorite salts, the hydantoin will be in granular form and will have particle size from about 12 to 100 mesh. For initiating preparation of the composition, as with the hypochlorite salt, it is preferred to start with a hydantoin in
15 granular form, e.g., to avoid dusting during blending.

In preparing the composition, there will be used from 75 to 99 weight percent of the hypochlorite salt and from 1 to 25 weight percent of the hydantoin, basis 100 weight percent of these ingredients. Use of less
20 than about 75 weight percent of the hypochlorite salt will be insufficient for providing desirable available chlorine. On the other hand, less than about 0.9 weight percent of hydantoin will be insufficient to provide beneficial effect from the hydantoin. These materials
25 in finely divided form, e.g., as granules, can then be brought together by any mixing means, preferably by mechanical mixing means which are typically utilized for forming blends of dry ingredients. These may include, for example, stirring and tumbling means or the like.
30 It is advantageous that mixing be carried out in such a manner that the particle size of the ingredients being mixed is not appreciably altered during the mixing of the dry materials. A preferred dry blending operation is accomplished with a ribbon blender. Particularly
35 where the blending is initiated with ingredients in very finely divided form, and the blending operation is to

form granules of the ingredients in mixture, there may be utilized a granulating operation, e.g., roller compacting of a moistened ingredient mix followed by granulating. By any manner of blending there will
5 result a solid, particulate composition which will typically have a highly desirable shelf stability on storage, e.g., as a packaged blend of particulate solids. In use, the particles may for example be simply mixed with a liquid medium for desired treatment, or the
10 liquid can flow by, e.g., through or over, the solid, water treatment blend particles.

It is to be understood that there may be present in the composition additional ingredients, such as binding agents, surface active agents, and the like.

15 For a representative composition there was blended together a commercial grade, granular calcium hypochlorite having a particle size between 16-40 mesh and containing 72-75 percent available chlorine. With this calcium hypochlorite there was blended a
20 commercially available, 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH). This commercial BCDMH was 93.5 percent active ingredient, with a balance of incidental inerts, having about 59 percent available chlorine and was a granular material having particle
25 size between 12-40 mesh. The blending was done for about 10 minutes in a double spiral blade ribbon blender. The resulting blend was a white granular solid and contained 5 weight percent BCDMH and 95 weight percent calcium hypochlorite, the water having been
30 essentially volatilized during the blending operation. This solid granular composition was 70 percent minimum active halogen, expressed as available chlorine. The pH of a 1 percent solution of this solid, granular mixture, as determined by dissolving 1 gram of the blend in 100
35 milliliters of deionized water, was 9.15 at 20° C.

CLAIMS

1. As a new composition of matter, a solid composition in the form of particles blended together of calcium hypochlorite and 1-bromo-3-chloro-5,5-dimethylhydantoin.
5
2. The composition of claim 1, wherein said solid composition is in the form of particles having size within the range of from about 12 to about 100 mesh.
3. The composition of claim 1, wherein said solid composition contains from 75 to 99 weight percent of said hypochlorite and from 0.9 to 25 weight percent of said hydantoin, basis 100 weight percent of these ingredients.
10
4. As a new composition of matter, a solid composition in the form of particles blended together of one or more alkali metal or alkaline earth metal hypochlorite with one or more N-halogenated dialkylhydantoin.
15
5. The composition of claim 4, wherein said solid composition is in the form of particles having size within the range of from about 12 to about 100 mesh.
20
6. The composition of claim 4, wherein said solid composition contains from 75 to 99 weight percent of said hypochlorite and from 0.9 to 25 weight percent of said hydantoin, basis 100 weight percent of these ingredients.
25

7. The composition of claim 4, wherein said hypochlorite is one or more of sodium, potassium, lithium, calcium or magnesium hypochlorite.

5 8. The composition of claim 4, wherein said hydantoin has N-chlorination, or N-bromination or both, and said alkyl groups are methyl, ethyl, or their mixtures.

10 9. The composition of claim 4, wherein said hydantoin is one or more of 1-bromo-3-chloro-5,5-dimethylhydantoin, 1, 3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin or 1,3-dichloro-5-ethyl-5-methylhydantoin.

15 10. The method of treating an aqueous medium to provide available chlorine thereto, which method comprises treating the medium with a solid composition of blended particles of one or more alkali metal or alkaline earth metal hypochlorite with one or more N-halogenated dialkylhydantoin.

20 11. The method of claim 10, wherein said solid composition of blended particles is admixed with said aqueous medium.

12. The method of claim 10, wherein said aqueous medium is flowed into contact with said solid composition of blended particles.

25 13. The method of claim 10, wherein said solid composition of blended particles treats an aqueous medium of one or more of sewage media, plant effluent, cooling tower liquid or secondary water media.

14. The method of claim 10, wherein said aqueous medium is treated with a solid composition of particles of one or more of lithium, calcium or magnesium hypochlorite blended with a hydantoin having N-
5 chlorination or N-bromination, or both, and having alkyl groups of one or more of methyl or ethyl.

15. The method of claim 10, wherein said aqueous medium is treated to supply both available chlorine and bromine thereto.